DEFECT THERMODYNIMCS AND LATTICE SITE BASICITY OF PROTON AND MIXED CONDUCTING OXIDES

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The extent of hydration of acceptor doped proton conducting oxides, typically described by dissociative hydration

$$\mathrm{H_2O(g)} + \mathrm{O_O^\times} + \mathrm{v_O^{\bullet\bullet}} \leftrightharpoons 2\mathrm{OH_O^\bullet} \quad (1)$$

has been correlated to various materials properties such as cation electronegativity and is argued to reflect the oxides' basicity. [1,2] The reaction is, however, amphoteric; lattice oxygen ions are protonated while oxygen vacancies are hydroxylated, suggesting that the extent of hydration rather is governed by the basicity of the lattice oxygen ions – and the acidity of the oxygen vacancies. Recently a number of mixed conducting perovskites with redox-active and typically more acidic elements on the perovskite's B-site have been shown to protonate according to

$$\mathrm{H_2O(g)} + 2\mathrm{O_O^\times} + 2\mathrm{h^\bullet} \leftrightharpoons 2\mathrm{OH_O^\bullet} + 1/2\mathrm{O_2(g)} \quad (2)$$

indicating that the hydration properties of *e.g.* novel cathode materials can be tailored by optimizing the oxide ion and vacancy basicity/acidity.

In this contribution we introduce the oxides' proton and hydroxide affinity (PA and HA) as a measure of the oxide ion basicity and vacancy acidity, respectively, and show how these parameters can be determined from first principles DFT calculations. The PA and HA, and thermodynamics of Eq. 1 are calculated for a selection of binary and perovskite structured oxides, and discussed in relation to the oxide's electronic, structural and bonding properties. The calculated affinities of the binary oxides generally follow the expected periodic trends and are shown to correlated with the position of the O2p bonding states, reflecting the relationship between the oxide's electronic structure and basicity. We furthermore assess a series of perovskite structured oxides and discuss correlations between their defect thermodynamics/ion affinities and electronic structure, basicity and A-O and B-O bond characteristics

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[1] T. Norby, M. Widerøe, R. Glöckner and Y. Larring, Dalton Transactions, 19, (2004)
[2] K.D. Kreuer, Annu. Rev. Mater. Res. 33 (2003) 333–59